



Photoelectrocatalytic degradation of refractory organic compounds enhanced by a photocatalytic fuel cell

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ABSTRACT

A novel composite photoelectrocatalytic system, composed of a photoelectrocatalytic reactor and a photocatalytic fuel cell (PFC), was established with the aim to efficiently degrade refractory organic compounds. The PFC is device, in which the organic “substrates” were photodecomposed and the chemical energy of organic “substrates” was converted into electrical energy simultaneously. Within the composite system, the electricity produced by PFC, rather than external power supply, was exerted on the photoelectrocatalytic reactor to serve as potential bias. The organic compound degradation performance and affecting factors of the composite system were also studied. The experimental results demonstrate that the removal efficiency of organic compound in the photoelectrocatalytic reactor was evidently enhanced by the PFC system. The kinetic constant of the photoelectrocatalytic process was found to be ~1.75 times that of the pure photocatalytic process. Furthermore, the performance of the photoelectrocatalytic reactor was found to increase with the illumination area (of the anode) of PFC and decrease with the external resistor and electrolyte concentration. The category and concentration of the substrate in PFC system were also key factors influencing the efficiency of organic compound removal in the photoelectrocatalytic reactor. The composite system provides a novel way for utilizing of the electrical energy generated from the PFC system and has potential applications for the treatment of various refractory organic pollutants.

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1. Introduction

Photocatalytic oxidation technique based on TiO₂ has been proven to be a promising process that can be used to degrade various persistent and hazardous organic pollutants, such as pharmaceutical compounds, aromatics, and azo dyes [1–4]. Upon illumination, photogenerated electrons are excited from the valence band to the conduction band; this generates electron-hole pairs. The positive holes are powerful oxidants for degrading the organic compounds adsorbed on the TiO₂ surface into CO₂ and H₂O [5–7]. However, as a typical n-type photocatalyst, TiO₂ is severely limited in practical applications due to its poor quantum yield, which is caused by rapid recombination of photogenerated electrons and holes. Application of a positive bias potential across the electrodes can greatly improve the photocatalytic efficiency by effectively separation of photogenerated charge carriers [8]. However, such an approach requires additional power supply and inevitably increases the cost of wastewater treatment. Therefore,

there is an urgent need to develop a cost-effective supply of external electricity for the practical applications of TiO₂-based photocatalytic/photoelectrocatalytic technologies [9].

Most studies on TiO₂-based photocatalysis have mainly focused on the efficiency and the extent of mineralization [10–12]. However, an equally important aspect of photocatalysis, energy recovery, has not received much attention. Furthermore, the organic compounds in wastewater are important sources of energy [13]. Approaches that recover the energy from these energy-rich organic wastes and degrade them to non-hazardous products are highly desirable. In response to these problems, designing a system in which organic compounds from wastewater are degraded and the chemical energy is converted into electrical energy simultaneously can achieve a double benefit – organic pollutant degradation and energy reclamation [14]. Since the TiO₂ photocatalytic process may degrade organic matter and constantly produce electrons that directly pass through the conductive substrate to the cathode, a TiO₂-based photocatalytic fuel cell (PFC) system is conceivable (Fig. 1). The PFC is device that use TiO₂-nanotube-array photocatalyst to oxidize organic “substrates” and generate current. Thus, it can be anticipated that the electricity generated from a PFC system could be used to supply additional bias potential to a

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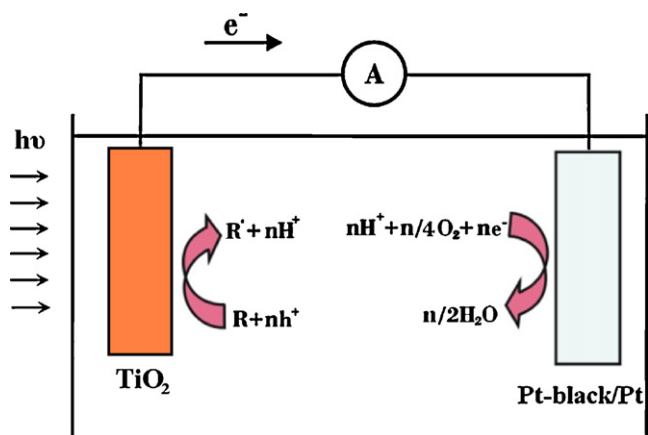


Fig. 1. Schematic diagram of working principle of the TiO_2 -based PFC system.

photocatalytic system to enhance the treatment efficiency of organic pollutants. Preparation by sonoelectrochemical anodization of a short, robust, and highly ordered TiO_2 nanotube array (STNA) with high electron transfer performance and excellent mechanical stability has been reported [15]. In the present work, a novel composite photoelectrocatalytic system was established with the aim to efficiently degrade refractory organic compounds, using tetracycline as a model compound. Since tetracycline is widely used in agriculture and maintenance of livestock, it can disrupt the ecosystem equilibrium (see Supporting Information) [16]. The composite system was composed of a photoelectrocatalytic reactor and a PFC, both based on the STNA electrode. The PFC was used to provide a bias potential, instead of external power supply, to the photoelectrocatalytic reactor to achieve effective removal of tetracycline. The present work may provide an efficient and cost-effective method to establish a PFC-assisted photoelectrocatalytic oxidation process of organic pollutants.

2. Experimental

2.1. Materials

Titanium sheets (0.25 mm thick, 99.9% purity) were supplied by Sumitomo Chemical (Japan). Unless otherwise indicated, reagents were obtained from the Sinopharm Chemical Reagent Company and were used as received. Tetracycline was purchased from Wuhan Yuancheng Technology Development Co., Ltd. All solutions were prepared using high-purity DI water.

2.2. Preparation of STNA

Details of the preparation of STNA have been published in previous work [15]. The anodized samples were rinsed with DI water and dried in air. Subsequently, the prepared STNA samples were crystallized by annealing in air for 3 h at 450°C , with heating and cooling rates of $1^\circ\text{C}/\text{min}$.

2.3. Apparatus

The layout and working principle of the composite system are shown in Fig. 3. The PFC was constructed in a rectangular quartz reactor ($20\text{ mm} \times 20\text{ mm} \times 50\text{ mm}$) employing a two-electrode system (an STNA photoanode and a Pt-black/Pt cathode). Unless otherwise stated, 10 mL of acetic acid solution (0.05 mol L^{-1}) with 0.1 mol L^{-1} Na_2SO_4 was used as the substrate.

The photoelectrocatalytic experiments were performed in a rectangular shaped quartz reactor ($20\text{ mm} \times 40\text{ mm} \times 50\text{ mm}$)

using an STNA photoanode and a Pt foil cathode, and a saturated Ag/AgCl was put into the reaction solution act as a reference electrode. The experiment on the degradation of tetracycline was performed under the following conditions: UV irradiation (2.0 mW cm^{-2} light intensity), pH 4.5, vigorous stirring, 0.01 mol L^{-1} Na_2SO_4 as electrolyte (except when 0.1 and 0.5 mol L^{-1} were used to evaluate the effect of solution ionic conductivity on the system performance), and $2\text{ cm} \times 3\text{ cm}$ illumination area of the photoanode. The initial tetracycline concentration was 0.045 mmol L^{-1} , and the reaction solution volume was 25 mL during the experiment. The reaction solution was analyzed in a spectrophotometer (UV2102 PCS, UNICO, Shanghai) at different time intervals at 355 nm. All runs were repeated at least three times to check their reproducibility.

The PFC and the photoelectrocatalytic reactor were connected in tandem with an external resistance ($10\ \Omega$, unless mentioned otherwise) between the photoanode of the photoelectrocatalytic reactor and the cathode of the PFC.

2.4. Methods

The circuit current was calculated from the voltage across the external resistance which was continuously recorded using a CHI electrochemical analyzer (CHI 660C, CH Instruments, Inc., USA). Linear sweep voltammetry (LSV) was conducted using the CHI electrochemical analyzer. The output voltage of the PFC and input voltage of the photoelectrocatalytic reactor were directly measured by a high-precision digital multimeter (Victor 98A, Shenzhen Victor Hi-tech Co., Ltd.). While the potential of anode and cathode in the photoelectrocatalytic reactor was tested using the digital multimeter with Ag/AgCl electrode as the reference electrode.

3. Results and discussion

3.1. Working principle of the PFC system

Fig. 1 illustrates the working principle of PFC system. Under illumination, photo-generated electrons are excited from the valence band to the conduction band of TiO_2 nanotubes, generating electron-hole pairs. The positive holes are powerful oxidants for degrading the organic substrates in the system. Photogenerated electrons move through an external circuit to the cathode. Hydrogen ions generated from photooxidation move toward the cathode by diffusing through the electrolyte solution. These are either reduced by externally arriving electrons producing molecular hydrogen under anaerobic conditions, or interact with oxygen and produce water under aerobic conditions. In both cases, an electric current flows between the anode and the cathode. The net effect of the PFC system is degradation of organics through the STNA photocatalytic process to produce electrical energy.

Fig. 2a shows the polarization plot for a typical PFC system composed of an STNA photoanode and a Pt-black/Pt cathode, using 0.05 mol L^{-1} acetic acid as substrate. The PFC system produces, under the present non-optimized conditions, an open-circuit voltage (V_{oc}) of $\sim 0.608\text{ V}$ and a short-circuit current (J_{sc}) of $\sim 0.261\text{ mA}$. The incident photon-to-current conversion efficiency (IPCE) for the present PFC system versus irradiated wavelength is shown in Fig. 2b. The highest IPCE value for the PFC system was 37% at $\sim 350\text{ nm}$, which can be interpreted both by the absorption band edge of the TiO_2 nanotubes (387.5 nm) and by the transmittance of the reactor decreasing at shorter wavelength than 350 nm [17].

3.2. Working principle of the composite system

The composite system contains an STNA-based PFC and an STNA-based photoelectrocatalytic reactor. Upon UV irradiation, the

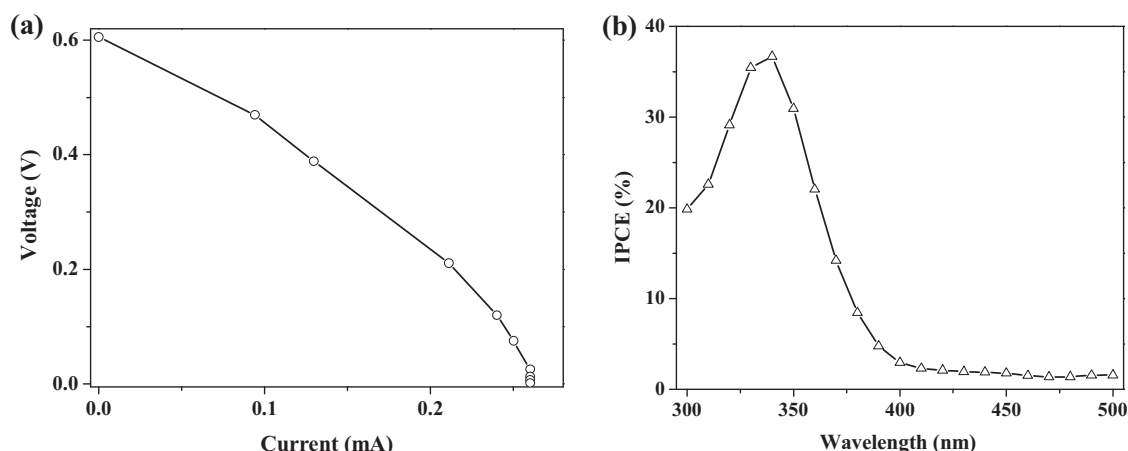


Fig. 2. (a) Voltage generated in the PFC system when the external resistance of the system is changed from 10 to 10,000 Ω ; (b) incident photon-to-current efficiency (IPCE) of a typical PFC system using 0.05 mol L⁻¹ acetic acid as substrate.

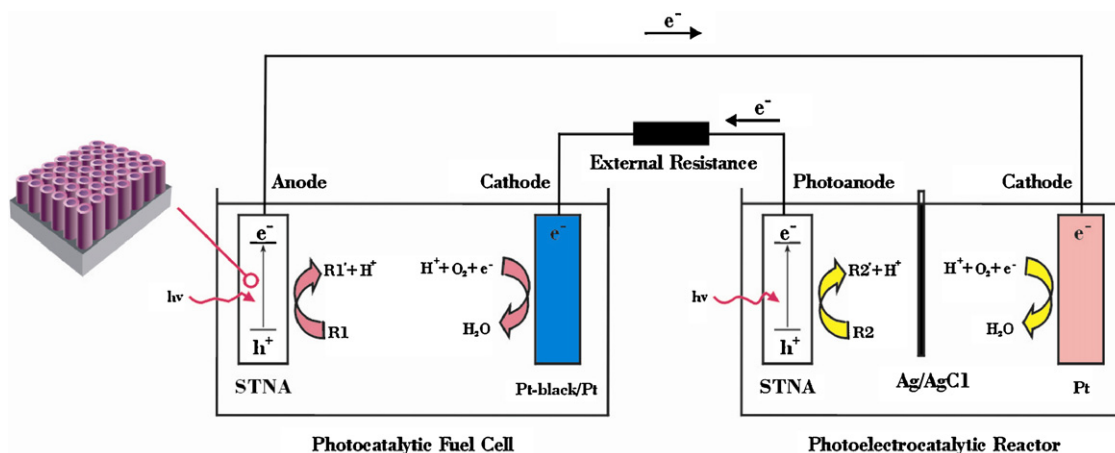


Fig. 3. Schematic diagram of the working principle of the composite system.

TiO₂ electrode in the PFC produces electron–hole pairs in the conduction band and valence band, respectively. The photogenerated holes will oxidize the organic substrate R1 into R1'. Hydrogen ions generated from photooxidation move toward the cathode by diffusing through the electrolyte solution. The photogenerated electrons move through an external circuit to the cathode of the photoelectrocatalytic reactor, while the STNA electrode in photoelectrocatalytic reactor oxidizes the organic compound R2 into R2'; this is followed by movement of electrons into the electrode. The electrons generated subsequently transfer to the cathode of the PFC, and they interact with oxygen and hydrogen ions to produce water under aerobic conditions. In this case, an electric current flows between the PFC and the photoelectrocatalytic reactor. This composite system is very attractive because it leads to efficient wastewater treatment through a cost-effective route. The PFC system serves as a power supply and provides an external anodic bias to the photoelectrocatalytic reactor for efficient degradation of organic pollutants. The main working principle of the composite system is presented in Fig. 3. The induced photocurrent and the electrochemical current of the photoelectrocatalytic reactor were compared by conducting the LSV test with and without UV illumination (Fig. 4). The electrochemical current was rather low in the absence of UV illumination. Compared with the results in the dark, the anodic current density under UV illumination demonstrates that the photocurrent can be effectively promoted by increasing the applied potential from 0.0 to 1.0 V.

3.3. Degradation of tetracycline

The electrochemical, direct photolytic, photocatalytic, and PFC-assisted photocatalytic (i.e. photoelectrocatalytic) processes of

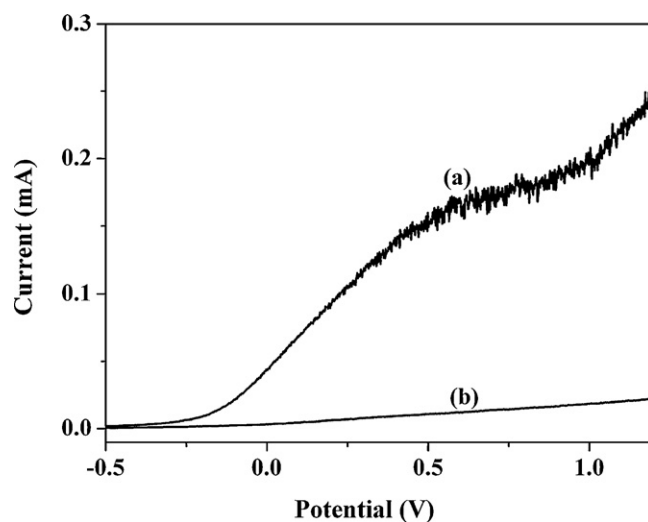


Fig. 4. Linear sweep voltammetric curves of the photoelectrocatalytic reactor in the presence (a) and absence (b) of UV light.

Table 1
Performance of the composite system under different conditions.

| Substrate | Photocatalytic fuel cell | | | $R (\Omega)$ | $J (\text{mA})$ | Photoelectrocatalytic reactor | | | $k (\text{h}^{-1})$ |
|---|----------------------------|-----------------------------------|--------------------------------|--------------|-----------------|-----------------------------------|--------------------------------------|-------------------------------|---------------------|
| | $V_{\text{oc}} (\text{V})$ | $\bar{V}_{\text{PFC}} (\text{V})$ | $A_{\text{PFC}} (\text{cm}^2)$ | | | $\bar{V}_{\text{PEC}} (\text{V})$ | $C_{\text{PEC}} (\text{mol L}^{-1})$ | $P_{\text{Anode}} (\text{V})$ | |
| – | – | – | – | 0 | – | – | 0.01 | – | 0.318 |
| Acetic acid (0.05 mol L ⁻¹) | 0.608 | 0.551 ± 0.015 | 1 × 1 | 10 | 0.086 | 0.550 ± 0.003 | 0.01 | 0.167 ± 0.001 | 0.555 |
| Acetic acid (0.05 mol L ⁻¹) | 0.608 | 0.546 ± 0.005 | 1 × 1 | 10 | 0.055 | 0.545 ± 0.003 | 0.1 | 0.170 ± 0.001 | 0.490 |
| Acetic acid (0.05 mol L ⁻¹) | 0.608 | 0.537 ± 0.002 | 1 × 1 | 10 | 0.032 | 0.537 ± 0.001 | 0.5 | 0.200 ± 0.002 | 0.406 |
| Acetic acid (0.05 mol L ⁻¹) | 0.608 | 0.531 ± 0.003 | 1 × 1 | 100 | 0.075 | 0.530 ± 0.002 | 0.01 | 0.148 ± 0.001 | 0.523 |
| Acetic acid (0.05 mol L ⁻¹) | 0.608 | 0.527 ± 0.010 | 1 × 1 | 1000 | 0.061 | 0.526 ± 0.005 | 0.01 | 0.167 ± 0.002 | 0.387 |
| Acetic acid (0.05 mol L ⁻¹) | 0.623 | 0.573 ± 0.001 | 1 × 3 | 10 | 0.10 | 0.573 ± 0.001 | 0.01 | 0.114 ± 0.002 | 0.586 |
| Acetic acid (0.05 mol L ⁻¹) | 0.639 | 0.603 ± 0.004 | 2 × 3 | 10 | 0.13 | 0.603 ± 0.003 | 0.01 | 0.083 ± 0.001 | 0.611 |
| Acetic acid (0.025 mol L ⁻¹) | 0.556 | 0.492 ± 0.001 | 1 × 1 | 10 | 0.040 | 0.491 ± 0.001 | 0.01 | 0.191 ± 0.001 | 0.409 |
| Acetic acid (0.01 mol L ⁻¹) | 0.491 | 0.442 ± 0.001 | 1 × 1 | 10 | 0.033 | 0.442 ± 0.001 | 0.01 | 0.201 ± 0.001 | 0.391 |
| Glucose (0.05 mol L ⁻¹) | 0.595 | 0.506 ± 0.002 | 1 × 1 | 10 | 0.042 | 0.505 ± 0.001 | 0.01 | 0.147 ± 0.001 | 0.418 |
| Urea (0.05 mol L ⁻¹) | 0.393 | 0.391 ± 0.001 | 1 × 1 | 10 | 0.030 | 0.391 ± 0.002 | 0.01 | 0.207 ± 0.002 | 0.386 |

Note: V_{oc} is the open-circuit voltage of the PFC, \bar{V}_{PFC} is the average output voltage of PFC within 3 h; A_{PFC} is the illumination area of the photoanode in PFC; R is the external resistance between the PFC and photoelectrocatalytic reactor and J is the electric current across the composite system; \bar{V}_{PEC} , C_{PEC} and P_{Anode} is, respectively, the average input voltage within 3 h, the concentration of supporting electrolyte and the average anode potential within 3 h in photoelectrocatalytic reactor. k is the reaction rate constant of tetracycline removal in the photoelectrocatalytic reactor.

tetracycline solutions were performed under the given conditions. The degradation of tetracycline evidently followed the Langmuir–Hinshelwood model (see Supporting Information). The electrochemical process was clearly much slower than the other processes (Fig. 5). Photolysis of tetracycline with UV light alone resulted in 16% tetracycline removal after 3 h. The presence of TiO₂ nanotubes resulted in degradation over 3 h. When an external anodic potential ($\sim +0.550 \text{ V}$) provided by the PFC system was applied to the photoelectrocatalytic reactor, the tetracycline removal ratio sharply increased to 81%. The ranking of the rate constant k of various processes was photoelectrocatalysis (0.555 h^{-1}) > photocatalysis (0.318 h^{-1}) > direct photolysis (0.057 h^{-1}) > electrochemical process (0.003 h^{-1}). The largest rate constant of the photoelectrocatalytic process may be

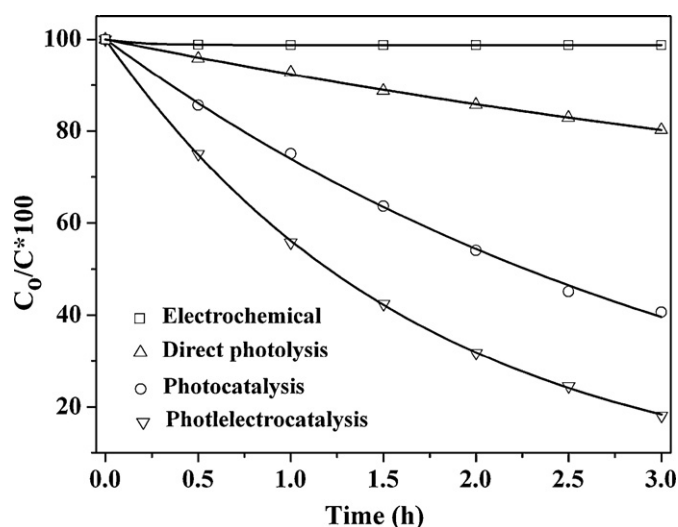


Fig. 5. Electrochemical process, direct photolysis, photocatalysis, and photoelectrocatalysis on an STNA electrode in tetracycline solutions.

ascribed to the suppression of the recombination of the photo-generated electron–hole pairs by the external electric field. The rate constant of photoelectrocatalysis was ~ 1.75 times as high as that for photocatalysis. Therefore, there was an obvious synergetic effect between the electrochemical process and the photocatalytic process.

The variation of current, voltage and electrode potential of the composite system under UV illumination is presented in Fig. 6. The current increased sharply initially, and then rapidly declined (Fig. 6a). The observed trends may be due to the change in output voltage of the PFC, which directly led to the change in input voltage of the photoelectrocatalytic reactor. In the initial few seconds, the output voltage of the PFC decreased from the open-circuit voltage (V_{oc}) to a relatively stable value, and the input voltage of the photoelectrocatalytic reactor changed accordingly. After UV illumination, the current considerably increased and then decreased slowly due to the generation of photocurrent and the removal of organic compounds. The PFC served as a power system, and the increase in the external current directly led to a decreased output voltage and subsequently a decreased input voltage of the photoelectrocatalytic reactor.

The potential of the electrodes in the photoelectrocatalytic reactor also changed after the change of the output voltage of the PFC. The average output/input voltage is depicted in Fig. 6b and is presented in Table 1. As can be seen, the average output voltage of PFC system (within 3 h) and the average input voltage of the photoelectrocatalytic reactor (within 3 h) were nearly overlapping with each other. This can be ascribed to the extremely low current value of the external circuit, which directly led to a very small voltage of the external resistance (within an order of 10^{-4} to 10^{-2} V). At $0.045 \text{ mmol L}^{-1}$ tetracycline and $0.01 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution with external resistance of 10Ω , the average potential at the anode (P_{Anode}) of the photoelectrocatalytic reactor was $\sim +0.167 \text{ V}$ and the average input voltage of the photoelectrocatalytic reactor was $\sim +0.550 \text{ V}$. The bias potential leads to the effective separation of photogenerated electron–hole pairs and thus the enhanced removal of tetracycline [18].

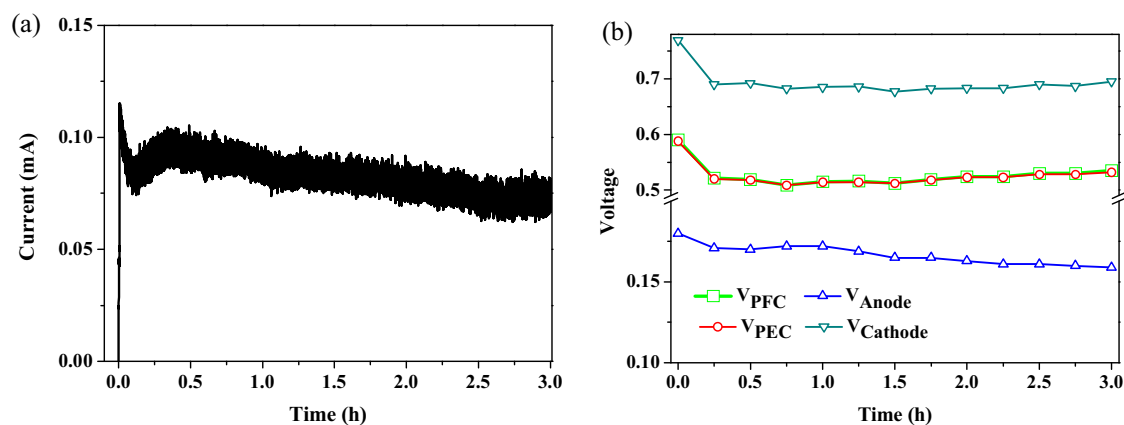


Fig. 6. (a) Variation of current of the composite system in a typical process of tetracycline degradation. (b) Variation of the output voltage of PFC, input voltage, and potentials of anode and cathode in the photoelectrocatalytic reactor.

Within the composite system, several half-reactions are involved: the organic compound degradation in the PFC, oxygen reduction in the cathodes of PFC and photoelectrocatalytic reactor as well as the organic pollutant degradation in the photoelectrocatalytic reactor, as shown in Table 2. These half-reactions can interact with each other and equilibrium among different reactions is expected in a stabilized system. For instance, in the PFC system, the hydrogen ions needed for cathodic reaction was came from the anodic reaction and the consumed electrons could come from the photoelectrocatalytic reactor. Moreover, some reactions cannot occur in the absence of the PFC or UV light. Without the PFC, a much lower rate constant of tetracycline degradation (0.318 h^{-1}) was obtained due to the high rate of recombination of photogenerated electrons and holes. Similarly, without the UV illumination for the photoelectrocatalytic reactor, the degradation rate was even lower. In that case, the photoelectrocatalytic reactor acted as an electrochemical reactor and no photogenerated holes were produced for tetracycline degradation. However, in the presence of the PFC and UV illumination, the current increases immediately accompanied with a markedly enhanced efficiency of pollutant removal in the photoelectrocatalytic reactor.

It should be also noted that the reaction occurring in the cathode of the photoelectrocatalytic reactor is also vital to the overall performance. The electrons generated from the anode of the PFC system will transfer to the cathode of the photoelectrocatalytic reactor and then consumed by oxygen reduction reaction to achieve electrically neutrality between the PFC system and the photoelectrocatalytic reactor. Therefore, the produced current by the composite system was closely related to anodic/cathodic reaction in the two sections and the effect of other important factors on the performance of the composite system will be discussed in the following section. Furthermore, within the composite system, both photoanodes in the PFC and in the photoelectrocatalytic reactor needs excitation by the incident UV light. This will inevitably consumes electrical energy. However, if the TiO_2 photoanodes can be modified by depositing noble metal on its surface, sensitizing it with dyes, or doping it with transition metals or non-metal elements and complexes with matching semiconductors, it will

directly absorbs visible light [3,18]. In that case, the proposed composite system can work outdoors efficiently under natural solar illumination, which will be the research focus in the next stage.

3.4. Performance of the composite system as affected by different parameters

Table 1 summarizes the performance of the composite system under various different conditions. The V_{oc} , \bar{V}_{PFC} and A_{PFC} are, respectively, the open-circuit voltage, the average output voltage within 3 h and the illumination area (of the photoanode) of the PFC system. While the \bar{V}_{PEC} , C_{PEC} , P_{Anode} and k represents the average input voltage within 3 h, the concentration of the supporting electrolyte, the average anode potential within 3 h and the rate constant for tetracycline removal in the photoelectrocatalytic reactor, respectively. Moreover, R denotes the external resistance between the PFC and the photoelectrocatalytic reactor and the J is the produced electric current across the composite system.

Within the composite system, the change of the circuit current passing through was directly related to the change of the output voltage of PFC system. Meanwhile, the output voltage of PFC was further determined by the potential of photoanode (STNA) and the potential of cathode (Pt-black/Pt). Since the potential of the cathode will keep constant ($\text{O}_2/\text{H}_2\text{O}$) during the reaction, the potential of the photoanode will strongly affect the produced circuit current within the composite system. Factors affecting the potential of the photoanode include the intrinsic property of the STNA electrode, the category and concentration of organic substrates and other parameters (e.g. temperature). As shown in Table 1, the V_{oc} of the PFC system keeps constant at a given concentration of the same substrate (0.608 V). While the V_{oc} and \bar{V}_{PFC} of different substrates was quite different. For instance, the V_{oc} of acetic acid, glucose, and urea of the same concentration (0.05 mol L^{-1}) was, respectively, 0.608, 0.595, 0.393 V. Meanwhile, the \bar{V}_{PFC} was 0.550, 0.505 and 0.207 V, respectively. The corresponding rate constant for tetracycline removal in the photoelectrocatalytic reactor was ranked as: acetic acid (0.555 h^{-1}) > glucose (0.418 h^{-1}) > urea (0.386 h^{-1}). This indicates that the composition and microstructure of the substrates will directly influence the electrode potential of the photoanode in PFC system. The acetic acid reveals better performance than glucose or urea, which may be partly due to the relatively lower redox potential of acetate [19]. Therefore, the acetic acid molecular can be readily oxidized by photogenerated holes and produce desirable cell performance. The effect of the composition and microstructure of the substrates on the potential of the photoanode still needs further systematic research.

Table 2
The electrode reactions within the composite system.

| In the PFC system | In the photoelectrocatalytic reactor |
|---|--|
| In the anode, $\text{TiO}_2 + h\nu \rightarrow \text{h}^+ + \text{e}^-$ | In the anode, $\text{TiO}_2 + h\nu \rightarrow \text{h}^+ + \text{e}^-$ |
| $\text{C}_2\text{H}_4\text{O}_2 + \text{H}_2\text{O} + \text{h}^+ \rightarrow \text{CO}_2 + \text{H}^+$ | $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8 + \text{H}_2\text{O} + \text{h}^+ \rightarrow$ |
| | $\text{CO}_2 + \text{H}^+ + \text{NH}_4^+$ |
| In the cathode, $\text{H}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{H}_2\text{O}$ | In the cathode, $\text{H}^+ + \text{O}_2 + \text{e}^- \rightarrow \text{H}_2\text{O}$ |

When the concentration of the substrate (e.g. acetic acid) in the PFC system changed, the electrode potential of the photoanode in PFC will change correspondingly. As given in Table 1, with the concentration of acetic acid decreases from 0.05 to 0.01 mol L⁻¹, the V_{oc} of the PFC decreased from 0.608 to 0.491 V, which can be further explained by the Nernst equation. Since the potential of the photoanode in the PFC system was closely related to the concentration of the redox state of the substrate. Hence, the higher concentration of the substrate, the lower potential of the photoanode (i.e. the larger output voltage of the PFC system). Meanwhile, the electric current within the composite system decreased from 0.086 to 0.033 mA and the rate constant for tetracycline removal in the photoelectrocatalytic reactor was 0.555, 0.409, and 0.391 h⁻¹ at the substrate concentrations of 0.05, 0.025, and 0.01 mol L⁻¹, respectively. The evidently enhanced rate constant for tetracycline removal in the photoelectrocatalytic reactor at higher substrate concentrations can be ascribed to the improved input voltage of the photoelectrocatalytic reactor, which favors the decrement of the recombination rate between photogenerated charge carriers. Besides, according to the thermodynamic theory, the temperature will also affect the electrode potential of the photoanode in the PFC system. All the above-mentioned factors will directly or indirectly influence the electric current of the composite system as well as the tetracycline removal performance.

The illumination area of the photoanode (A_{PFC}) in the PFC, as one of the intrinsic properties of the STNA electrode, was also a significant factor influencing the electrode potential of the PFC system as well as the tetracycline removal efficiency in the photoelectrocatalytic reactor. Three illumination areas ($1 \times 1 \text{ cm}^2$, $1 \times 3 \text{ cm}^2$ and $2 \times 3 \text{ cm}^2$) were studied in the present work. The removal rate of tetracycline increased as the illumination area of the anode increased from $1 \times 1 \text{ cm}^2$ to $2 \times 3 \text{ cm}^2$ (Table 1). Around 85% tetracycline was removed when the illumination area was $2 \times 3 \text{ cm}^2$; this is higher than the ~4% tetracycline removal rate obtained using an area of $1 \times 1 \text{ cm}^2$. The ranking of areas according to the resulting rate constants was $2 \times 3 \text{ cm}^2$ (0.611 h^{-1}) > $1 \times 3 \text{ cm}^2$ (0.586 h^{-1}) > $1 \times 1 \text{ cm}^2$ (0.555 h^{-1}). With the increase in the illumination area of the PFC photoanode, more electrons could be generated under the same illumination intensities, as confirmed by the enhanced output voltage of the PFC and input voltage of the photoelectrocatalytic reactor (Table 1). This contributed to the lowered rate of recombination of photogenerated charges and to the higher efficiency of tetracycline removal.

With an increase in the external resistance (R) in the composite system, the output voltage of the PFC and the input voltage of the photoelectrocatalytic reactor decreased. This led to a decreased efficiency of tetracycline treatment because of the increased rate of recombination of photogenerated charges. When the external resistance between the PFC and the photoelectrocatalytic reactor increased from 10 to 1000 Ω with 0.01 mol L⁻¹ Na₂SO₄ as supporting electrolyte, the produced current was decreased from 0.086 to 0.061 mA and the rate constant for tetracycline removal decreased from 0.555 to 0.387 h⁻¹ accordingly.

In a typical catalytic process, the selection and concentration of the electrolyte solution is also very important [20]. In this study, Na₂SO₄ was selected as the electrolyte in the photoelectrocatalytic reactor, and three concentrations (0.01, 0.1 and 0.5 mol L⁻¹) were used to investigate the influence of electrolyte concentration at a constant external resistance of 10 Ω . The rate of tetracycline removal decreased when the electrolyte concentration increased from 0 to 0.5 mol L⁻¹. The rate constant was 0.555, 0.490, and 0.406 h⁻¹ at electrolyte concentrations of 0, 0.1, and 0.5 mol L⁻¹, respectively (Table 1). Meanwhile, the electric current was decreased from 0.086 to 0.032 mA. This phenomenon can be explained by the increased conductivity of the solutions that decreased the external resistance of the composite system and thus

reduced input voltage of the photoelectrocatalytic reactor. Since increasing of the conductivity will decrease the transfer resistance of photogenerated electrons within the photoelectrocatalytic reactor and the total resistance of the composite system was decreased accordingly. Therefore, based on Ohm's law, the decreasing of the external resistance will lead to the reducing of the input voltage of the photoelectrocatalytic reactor. Thus, a lower potential bias applied on the photoelectrocatalytic reactor enhanced the rate of recombination of photogenerated electron-hole pairs and reduced the efficiency of tetracycline removal.

4. Conclusions

A novel composite system composed a coupled photoelectrocatalytic reactor and a PFC was established. The PFC was used to provide an external bias potential to the photoelectrocatalytic reactor to achieve effective removal of tetracycline. The results demonstrate a synergetic effect between the electrochemical and photocatalytic processes. The external resistor, electrolyte concentration, illumination area of the anode, and category and concentration of the substrate in PFC were found to be important factors influencing the produced electric current of the composite system as well as the tetracycline removal performance in the photoelectrocatalytic reactor. The experimental results suggest that the proposed composite system may provide a promising solution to develop a PFC-assisted photoelectrocatalytic oxidation process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2011.10.038.

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